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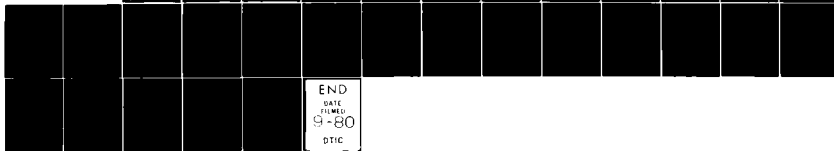
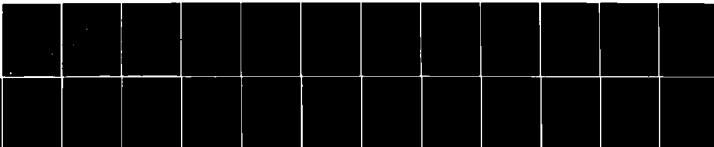
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Photoassisted Water-Gas Shift Reaction
over Platinized TiO_2 Catalysts*

by

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**Photoassisted Water-Gas Shift Reaction
over Platinized TiO₂ Catalysts***

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Abstract

The reaction of gas phase water with CO (water-gas shift reaction) over platinized, powdered TiO₂ is found to be catalytic under UV illumination. The reaction kinetics have been studied at temperatures from 0 to 60°C. At 25°C, the reaction is zero order both in CO and H₂O when $p_{CO} \geq 0.3$ torr and $p_{H_2O} \geq 5$ torr and the activation energy is 7.5⁶⁰ kcal/mole. The wavelength dependence of the reaction rate shows a cut-off near, but slightly below, the band gap of TiO₂. The quantum efficiency of the reaction is about 0.5% at 25°C. A mechanism is proposed which involves the photodecomposition of H₂O over platinized TiO₂.

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I. Introduction.

Heterogeneous photocatalysis is a relatively new branch of catalysis and in almost all cases semiconductors are used because band-gap photon absorption leads to spatially separated electrons and holes which can be used in oxidation-reduction reactions [1]. Metallized semiconductors have recently appeared which are more effective in some cases than semiconductors alone. For example, Bulatov and Khidekel [2] have reported the photodecomposition of acidified water using platinized TiO_2 (Pt/TiO_2). Kraeutler and Bard [3] have reported the selective decomposition of liquid acetic acid to methane over illuminated Pt/TiO_2 . In the gas phase, Hemminger et al. [4] have claimed the photocatalytic production of methane from CO_2 and gaseous H_2O using a SrTiO_3 crystal contacted with a Pt foil.

We have recently begun to investigate the photocatalytic properties of TiO_2 and Pt/TiO_2 , and have found that UV-illuminated Pt/TiO_2 , but not TiO_2 alone, catalytically decomposes liquid H_2O [5]. Platinized TiO_2 also photocatalyzes the reactions of gaseous H_2O with hydrocarbons [6], active carbon [6] and lignite [7] to produce H_2 and CO_2 , all of which are thermodynamically unfavorable. We report here another photoassisted reaction over Pt/TiO_2 , the reaction of gaseous H_2O with CO (water-gas shift reaction). Although this reaction is not thermodynamically uphill ($\Delta G^\circ = -6.8 \text{ Kcal/mole}$) over illuminated Pt/TiO_2 , we believe it does involve the photodecomposition of water. Thus the present study, in addition to having intrinsic interest, serves to promote our understanding of thermodynamically unfavorable processes over illuminated Pt/TiO_2 .

The purpose of this article is to demonstrate that the photoassisted water-gas shift reaction can be catalytically accomplished over platinized titania at room temperature and that a mechanism which is compatible with the data involves the photodecomposition of water. It is not possible to establish clearly many of the molecular level details of this reaction. This awaits further experimentation involving the combination of optical and electron spectroscopic techniques.

2. Experimental Section.

TiO₂ (anatase) was obtained from MCB, doped in flowing H₂ for 6 hr at 700°C, cooled in H₂ and stored in a sample vial. Hydrogen was used after passage through a molecular sieve trap at liquid N₂ temperature. Platinized TiO₂ (~2 wt% Pt) was prepared by the photolysis of hexachloroplatinate dissolved in a Na₂CO₃-acetic acid buffer solution [8]. After photolysis the sample was washed with distilled water until Cl⁻ could not be detected and then was dried in a desiccator. The BET surface area of Pt/TiO₂ was about 11 m²/g. Oxygen-18 H₂O (99.3%) was obtained from Prochem. Carbon-13 CO (90%) [9] was used after passing through a liquid-N₂ trap.

The apparatus consisted of a vacuum system (base pressure 1×10^{-7} torr), a gas handling system, a reaction system (180 ml volume) and a gas analysis system, most of which were made of Pyrex glass. The reaction system was equipped with a circulation pump, a quartz reaction cell and a storage tube of distilled water which was outgassed several times at dry ice temperature.

The catalyst (0.25 g) was spread uniformly on the flat bottom of the reaction cell and outgassed for 3 hrs at 200°C. When studying the water-gas shift reaction, CO was introduced into the reaction system and circulated through the water storage tube to supply water vapor. When low H₂O pressures were needed, the water storage tube was cooled to a temperature at which the desired H₂O vapor pressure was obtained. During reaction the tube was isolated from the reaction system. After

setting the reaction cell temperature with a water bath, the catalyst was illuminated with a 200 W high pressure Hg lamp that was filtered through a quartz cell filled with NiSO_4 solution to remove heat. The gas mixture was sampled at various times, and after passage through a cold trap at about -110°C to remove H_2O , was analyzed by a mass spectrometer (CEC 21-614). The sensitivity of the mass spectrometer for each gas was calibrated using a gas mixture of known composition.

3. Results.

3.1 Reaction of gas phase H_2O with doped TiO_2

The hydrogen-doped TiO_2 (without Pt) used in the present experiments reacts with gaseous H_2O to produce H_2 under UV illumination at room temperature. This reaction was accompanied by the production of a small and variable amount of CO_2 which we believe arises from the photodecomposition of adsorbed carbonate. The rate of H_2 formation dropped to zero after a 2 hr.-irradiation and the maximum amount of H_2 formed was about 3×10^{-7} mole. This reaction was not affected by the presence of CO (i.e. the water-gas shift reaction did not take place) but was completely retarded by the addition of 3×10^{-2} torr of O_2 . Hydrogen was also produced when the TiO_2 was heated in gaseous H_2O at temperatures above $300^\circ C$. These results suggest that the H_2 formation arises from the activated and non-catalytic reaction of H_2O with a strongly reduced form of TiO_2 , such as Ti_2O_3 or TiO [10].

3.2 Reaction of H₂O with Pt/TiO₂

When Pt/TiO₂ was illuminated in the presence of gaseous H₂O, H₂ and CO₂ were formed with concomitant formation of a small amount of CH₄. As shown in Fig. 1, the use of H₂¹⁸O instead of ordinary H₂O revealed that a part of the oxygen in CO₂ comes from H₂O. The ratio of (H₂ + 2CH₄) to (C¹⁸O₂ + 1/2 C¹⁶O¹⁸O) is nearly 2:1, suggesting that H₂O is photo-decomposed on Pt/TiO₂ and that the oxygen formed reacts with adsorbed carbon and CO. These carbon-containing species are probably present as the result of acetic acid decomposition during the preparation of Pt/TiO₂. The stoichiometric reaction of H₂O with doped TiO₂, described in section 3-1, should not contribute to these results since it will have gone to completion during the catalyst preparation. Oxygen atom exchange between H₂O and CO₂ present originally on TiO₂ may contribute a small amount to the observed C¹⁶O¹⁸O. Hydrogenation of adsorbed carbon will account for the formation of CH₄.

From Fig. 1 the maximum yield of H₂ is certainly larger than 0.09 torr (8.7 x 10⁻⁷ mole). This is a factor of three larger than the maximum H₂ yield found for TiO₂ and suggests that the addition of Pt increases the activity for H₂ production perhaps through a reaction pathway involving the decomposition of water.

If the photodecomposition of H₂O is indeed involved, H₂ should be continuously formed by the addition of some material, such as CO, which has a strong affinity for oxygen and forms a nonreactive product, such as CO₂. On this basis we tested for, and found, catalytic activity for the water-gas shift reaction on Pt/TiO₂.

3.3 Water-Gas Shift Reaction.

General Features. Figure 2 shows a typical time evolution of the water-gas shift reaction over UV-illuminated Pt/TiO₂ at 25°C. Carbon-13 CO (0.6 torr total, 0.54 torr ¹³CO) was used in order to discriminate against the CO₂ yield that occurs in the absence of CO (g), see Fig. 1. The water pressure was 24 torr. Taking the isotopic purity of CO (90% ¹³C) into account, the stoichiometry of the shift reaction is well satisfied; $-\Delta p_{\text{CO}} = \Delta p_{\text{CO}_2} = \Delta p_{\text{H}_2}$. In the dark, the reaction rate was very slow at room temperature and, at 60°C, its contribution was only 0.6% of the photo-process. According to Fig. 2, the production of H₂ proceeds with no marked loss of activity until the carbon monoxide is consumed. Once the CO (g) is gone, however, the activity drops sharply to zero. In fact the H₂ pressure passes through a maximum indicating that some H₂ is consumed in the latter stages of the experiment summarized in Fig. 2. In this case the maximum amount of H₂ is 5.8×10^{-6} mole (1.3×10^{18} molecules m⁻² of catalyst).

As shown in Fig. 2, a small amount of O₂(g) appears as the pressure of CO drops below 0.06 torr. This pressure gradually increases at the end of reaction and then abruptly jumps to about 10⁻² torr when the CO pressure drops below 0.01 torr. No other products were detected in this experiment. The same was true for other reaction temperatures between 0 and 60°C.

Reproducibility. The photocatalytic activity was reproducible in a series of runs when the reaction was stopped and the system was evacuated before the CO pressure dropped below about 0.1 torr. If the reaction proceeded to completion, as in Fig. 2, an activity increase

was sometimes observed upon repeating the reaction after evacuation for only a few minutes. Outgassing for extended periods, even at room temperature, restored the activity to a reproducible value. In our experiments reproducible and stable activity was achieved after any experiment by outgassing at 150°C for one hour.

Pressure Dependence at 25°C. Figure 2 shows that the rate of the photoassisted water-gas shift reaction is almost constant until the pressure of CO falls to about 0.3 torr. Over this range there is a zero order dependence of the rate on CO pressure. Since the pressure of H₂O (24 torr) is much higher than the CO pressure (0.6 torr) the effect of its change during the reaction is negligible. The reaction accelerates slightly as the CO pressure drops below 0.3 torr indicating a slightly negative order in p_{CO} between 0.3 and 0.1 torr. Near completion the rate slows as the CO pressure drops implying a positive order in p_{CO} . These qualitative dependences were confirmed in a series of experiments utilizing initial CO pressures from 0.1 to 0.6 torr.

A slight increase in the initial rate (10 to 20%) was observed when the H₂O pressure was reduced from 24 torr to about 5 torr while the initial CO pressure was fixed at about 0.6 torr. The reaction is, therefore, almost zero order in H₂O pressure.

Temperature Dependence. Figure 3 shows the time dependence of the reaction at 0°C. The reaction rate is nearly constant over the entire pressure range observed though a slight decline is observed as the CO pressure drops below 0.25 torr. The consumption

of CO exceeds slightly the formation of H_2 probably due to CO adsorption on the catalyst during the reaction. The CO_2 production rate (not shown) equals the H_2 production rate.

At $60^\circ C$ (Fig. 4) the time evolution is qualitatively like that at $25^\circ C$; an initial constant rate followed by an acceleration at intermediate CO pressures and a retardation at the end of the reaction. However, the CO pressure at which the acceleration begins is higher than in the reaction at $25^\circ C$. The decline of the rate is not due to a loss of the photocatalytic activity of Pt/TiO_2 because the initial rate was reproduced in the next run. When the initial pressure of CO was reduced to 0.5 torr the rate accelerated earlier than in Fig. 4 and the retardation period became shorter. The reaction course at $40^\circ C$ showed a pattern intermediate between those at $25^\circ C$ and $60^\circ C$.

Figure 5 shows an Arrhenius plot of the reaction rates for temperatures from 0 to $60^\circ C$ in the region where the reaction takes place at a constant rate. The activation energy is 7.5 Kcal/mole, which is about the same as estimated for the photoassisted decomposition of liquid water (~ 5 kcal mole $^{-1}$) [5].

Wavelength Dependence. The wavelength dependence was qualitatively measured using three cut-off filters: a commercial UV cut-off filter (415 nm cut-off), a Plexiglass filter (3 mm thick, about 380 nm cut-off) and a Pyrex glass filter (3 mm thick, about 275 nm cut-off). As seen from Fig. 6, the 415 nm cut-off filter completely retarded the reaction while the Plexiglass and Pyrex filters suppressed the rate to 4 and 67%, respectively. There was no difference in the wavelength dependence at 25 and $60^\circ C$.

Formation of O_2 . The formation of O_2 during the water-gas shift reaction is surprising in the sense that it is not favored thermodynamically. The fact that it is formed may help in understanding the mechanism of the photoassisted water-gas shift reaction over Pt/TiO₂.

Typical pressure versus time curves for CO, H₂, CO₂ and O₂ are shown in Fig. 7. The amount of O₂ is very small (less than 5×10^{-4} torr) and almost constant in the region where the reaction takes place at a constant rate. After the shift reaction accelerates, O₂ gradually increases and then maximizes rather abruptly as CO drops below 0.01 torr. At the same time, the H₂/CO₂ ratio deviates sharply from unity and the excess of H₂ over CO₂ is about twice the amount O₂ formed, suggesting the decomposition of H₂O. The back reaction occurs readily over Pt and Fig. 7 suggest that the rate of this process increases when the CO pressure drops below 10^{-3} torr. The H₂ consumption rate observed here is much lower than the H₂ oxidation rate on a Pt/TiO₂ surface not exposed to CO [5]. As shown in Fig. 7, the rate becomes a little faster after the light is turned off

and turning the light source back on produces small amounts of O₂ and H₂. This O₂ formation pattern was reproducible although the quantitative amounts of O₂ produced in each region are sensitive to the activity of Pt/TiO₂, the reaction temperature and the initial CO pressure. The maximum amount of O₂ formed (t = 25 min. in Fig. 7) is not exactly reproduced but tends to decrease as the reaction temperature increases, as the activity decreases or as the initial CO pressure is raised.

Preparation Method Dependence. The Pt/TiO₂ prepared from undoped TiO₂ (no H₂-treatment) showed much lower ($\approx 10\%$) photocatalytic activity than the Pt/H₂-doped TiO₂ for the water-gas shift and the water decomposition reaction. The activity depends upon the conditions of the H₂-doping of TiO₂ (temperature, time and a flow rate of H₂). A strongly reduced TiO₂ leads to higher activity but an optimum condition was not established. As doping proceeds, TiO₂ changes color from white to light blue, indicating the production of a reduced form of TiO₂. Preliminary ESCA spectra of the doped and undoped forms revealed no detectable differences. The Pt loading may also affect the photocatalytic activity but this was not examined in the present study.

4. Discussion.

Our experiments show that the photoassisted water-gas shift reaction over Pt/TiO₂ is catalytic when the catalyst is irradiated with band-gap radiation. The reaction may involve photo-induced electronic processes similar to those noted in photoelectrochemical (PEC) cells [11] or photoelectrochemical diodes [12].

At the Pt-TiO₂ junctions formed by deposition of Pt, the valence and conduction bands will be bent upwards, because charge transfer will occur to equalize the Fermi levels of these materials. The extent to which this occurs for our catalyst cannot be readily determined because the doping level of TiO₂ is unknown, because the electronic coupling between TiO₂ and Pt is not known and because the Pt particles are small and not fully characterizable by bulk parameters. Upon irradiation and excitation of an electron into the conduction band of TiO₂, charge separation will compete with hole-electron recombination. Holes will tend to migrate to the Pt-TiO₂ interface and the electrons will migrate away from it. When a photostationary state is reached, the bending of the valence and conduction bands in the semiconductor will be reduced and the electrons and holes can be characterized by quasi-Fermi levels [11].

As a result of these photovoltage effects, we expect (1) that recombination of electrons and holes will become relatively more important than would be expected on the basis of the "dark" energy level diagram, (2) that holes will be found at both the Pt/TiO₂ and the TiO₂/gas interfaces and (3) that electrons will be captured at the Pt particles. If so, the photocatalyzed processes we have observed here can be described using the diagram (analogous to a shorted electrochemical cell [13]) shown in Fig. 8.

In this mechanism, holes come to the TiO_2 /gas interface where they react with adsorbed water to form an adsorbed OH radical and a proton. The latter diffuses to the Pt, probably mediated by the physisorbed water that is present, where it is reduced. When CO is present, it reacts with the OH radical to give CO_2 and a hydrogen atom which recombines with other hydrogen atoms at Pt sites. In the absence of CO, the adsorbed OH radical will either react with a second hole to form H^+ and a chemisorbed oxygen atom or two OH radicals will recombine to form H_2O_2 . Gas phase oxygen would then be formed either by recombination of oxygen atoms or by the rapid decomposition of H_2O_2 . The back reaction, $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$, occurs readily on Pt [14] and even occurs when liquid water is present [5], but at a slower rate. Consequently, in the absence of CO no measurable O_2 is evolved. In this case the only way a net amount of H_2 is evolved is to use surface carbon, present on the catalyst as a result of preparative techniques, to scavenge oxygen and make CO_2 (See Fig. 1).

The above descriptive mechanism is also applicable to the photolysis of liquid phase water on Pt/ TiO_2 [5] where the photodissocia-

tion rate is more competitive with the back reaction. There is, however, a problem in view of the fact that the Pt/TiO₂ PEC cell requires an external potential for water decomposition [11,15]. The reason for this requirement is not obvious. There are conflicting views regarding the position of the flat band potential

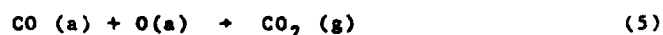
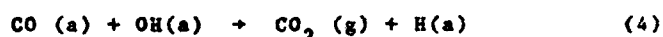
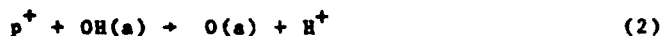
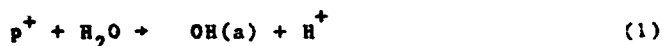
of TiO₂ with respect to the H⁺/H₂ redox potential. It has been reported as 50 mv positive [11] and 100 mv negative [16]. In the former case, electrons arriving at the Pt electrode of a PEC cell, must pass an energy barrier to reduce protons to hydrogen (this assumes the pressure is 1 atm). In the latter case, the reaction should occur under short circuit conditions. In either case, overvoltages and other voltage drops will contribute to the inefficiency and to the external potential requirements.

Our results, including those for liquid water [5], show that this reaction does occur without an external potential when the solid photoactive material involves small Pt particles dispersed on powdered TiO₂. One of the more important differences between our experimental conditions and those in PEC cells is the pressure. The total pressure in our experiments lies between 20 and 25 torr and the hydrogen pressure never exceeds 0.7 torr. The H⁺/H₂ redox potential under these conditions will certainly become more positive with respect to the TiO₂ flat band potential, and will allow the reaction to proceed more efficiently. Other differences must also be considered: (1) There will be more surface defects on powdered TiO₂ than on crystalline samples; the attending defect electronic states may be important. (2) The small Pt particles present on our catalyst may have electronic properties different from bulk Pt. (3) Unlike PEC cells, potentially significant [17]

direct chemical bonding between Pt and TiO_2 may be present here. The importance of each of these cannot be established on the basis of our data.

Another significant factor in the activity of the solid phase is the reduction of the TiO_2 in the preparation procedure. As noted by Wrighton et. al.¹⁵, this is important in photoelectrochemical cells. One reason is the lower resistivity of the H_2 -doped TiO_2 which enhances photoconductivity. We expect this same change in conductivity to be important in our powdered catalysts. Changes in electronic band structure upon creation of oxygen vacancies are also expected but this can not be examined by kinetic methods. Enhancement of the adsorption of reacting species on the reduced TiO_2 surfaces does not appear to be important.

Focussing now on the water-gas shift reaction, we note that the photodriven dissociation of water is indeed implicated since O_2 evolution is noted (Figs. 2, 4 and 7). Assuming such a model, the reaction steps probably include:



The intermediates are either denoted in Fig. 8 or described in the text that accompanies it. It is not clear whether Pt participates in steps (3), (4) and (5) since it may be covered with

H_2 during the reaction, as observed in the hydrogen electrode reaction over Pt dispersed on graphite [18].

The time-course of the water-gas shift reaction consists of three regions: (1) region 1 where the pressure of CO is relatively high and the reaction occurs at a constant rate, (2) region 2 where the reaction gradually accelerates with time and (3) region 3 where the depression of the rate and the formation of O_2 are observed (Figs. 2, 4 and 7).

When the CO pressure is high (region 1), the CO coverage on the catalyst surface would be saturated so that the reaction rate is dependent of the CO pressure. We believe this coverage on Pt inhibits H_2 evolution as observed in the reaction of water with active carbon [19] and lignite [7] over illuminated Pt/TiO₂. The coverage of CO on Pt begins to decrease when the CO pressure is reduced below a certain temperature dependent value. As a result, the reaction rate accelerates (region 2). When the CO pressure is low (region 3), the diffusion of CO through the layer of physisorbed water on TiO₂ may limit the rate (step 3). As a result the overall reaction rate is suppressed and the coverage of $O(a)$ may increase so that O_2 is produced. Some strongly adsorbed CO would however remain on Pt even after the gaseous CO is consumed and tend to inhibit the reaction of O_2 with H_2 . This adsorbed CO may be slowly removed and allow the back reaction to occur more rapidly (Fig. 7).

When the reaction temperature is increased, the amount of CO adsorbed on Pt will drop for a given CO pressure. Accordingly, acceleration of the shift reaction starts at higher CO pressures as indicated in Figs. 2-4. The migration of H(a) and O(a) on the catalyst surface, which results in their reaction to form H_2O , may become important at the end of the reaction at $60^\circ C$ (Fig. 4).

The reaction order with respect to CO pressure is thus explained in terms of the inhibition by CO (zero and negative order) and the CO diffusion (positive order). The zero order dependence of the rate on H_2O pressure is reasonable since the catalyst surface would be covered with physisorbed H_2O even at relatively low H_2O pressures.

The wavelength dependence of the rate is similar to the wavelength response of the photocurrent in a Pt/W-doped TiO_2 PEC cell studied by Wrighton *et.al.* [15]. According to their results, a TiO_2 electrode shows a photocurrent threshold near 400 nm and a saturation near 350 nm, while the onset of W-doped TiO_2 is shifted to shorter wavelengths by nearly 50 nm; H_2 -doping and platinizing TiO_2 may have a similar effect.

The quantum efficiency of the present reaction is low (about 0.5% in region 1 at room temperature). This may be improved by changing the level of H_2 -doping and the Pt loading.

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Figure Captions

Figure 1

Products of the reaction of H_2^{18}O with Pt/TiO_2 under UV illumination. $p_{\text{H}_2^{18}\text{O}} \approx 24$ torr.

Figure 2

Time course of the water-gas shift reaction over illuminated Pt/TiO_2 at 25°C . $p_{\text{H}_2\text{O}} \approx 24$ torr.

Figure 3

Time course of the photoassisted water-gas shift reaction over Pt/TiO_2 at 0°C . Plots of CO_2 are omitted as they almost overlap on the plots of H_2 . $p_{\text{H}_2\text{O}} \approx 5$ torr.

Figure 4

Time course of the photoassisted water-gas shift reaction over Pt/TiO_2 at 60°C . Plots of CO_2 almost overlap on those of H_2 . $p_{\text{H}_2\text{O}} \approx 24$ torr.

Figure 5

Arrhenius plot of the rates of photoassisted water-gas shift reaction over Pt/TiO_2 . $p_{\text{CO}} = 0.5 \sim 0.6$ torr, $p_{\text{H}_2\text{O}} \approx 24$ torr (as above at 0°C).

Figure 6

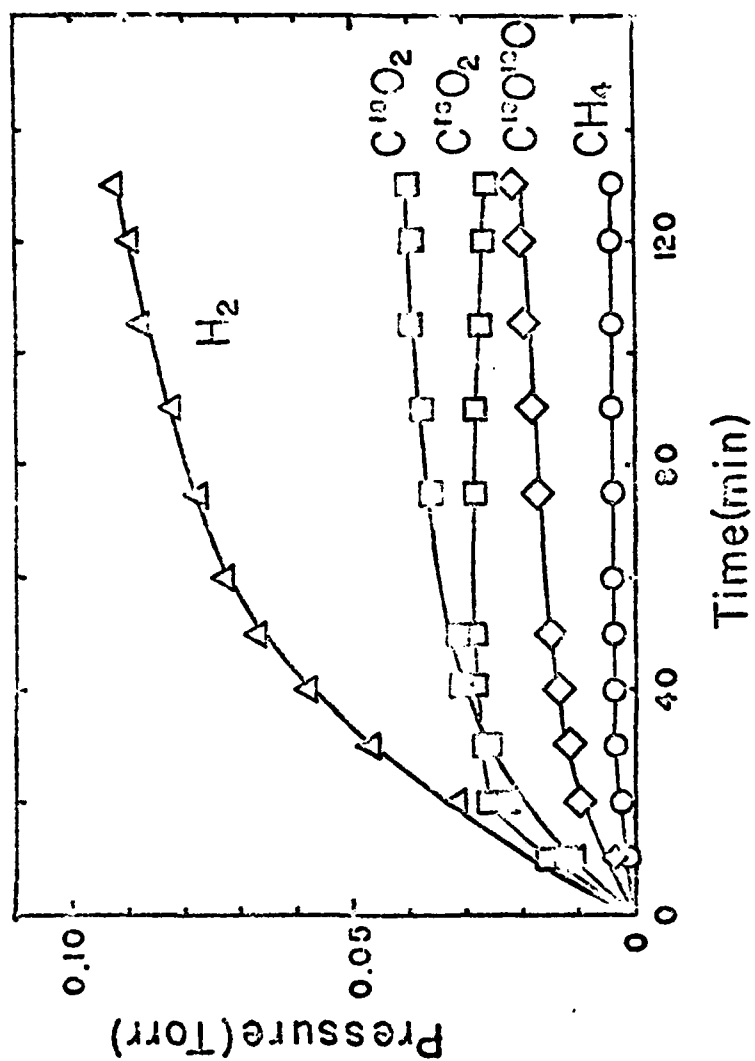
Effects of cut-off filters on the rate of photoassisted water-gas shift reaction over Pt/TiO_2 at 25 and 60°C . $p_{\text{H}_2\text{O}} \approx 24$ torr, $p_{\text{CO}} = 0.5 \sim 0.6$ torr.

Figure 7

Formation of O_2 during the photoassisted water-gas shift reaction over Pt/TiO_2 at 25°C . $p_{\text{H}_2\text{O}} \approx 24$ torr.

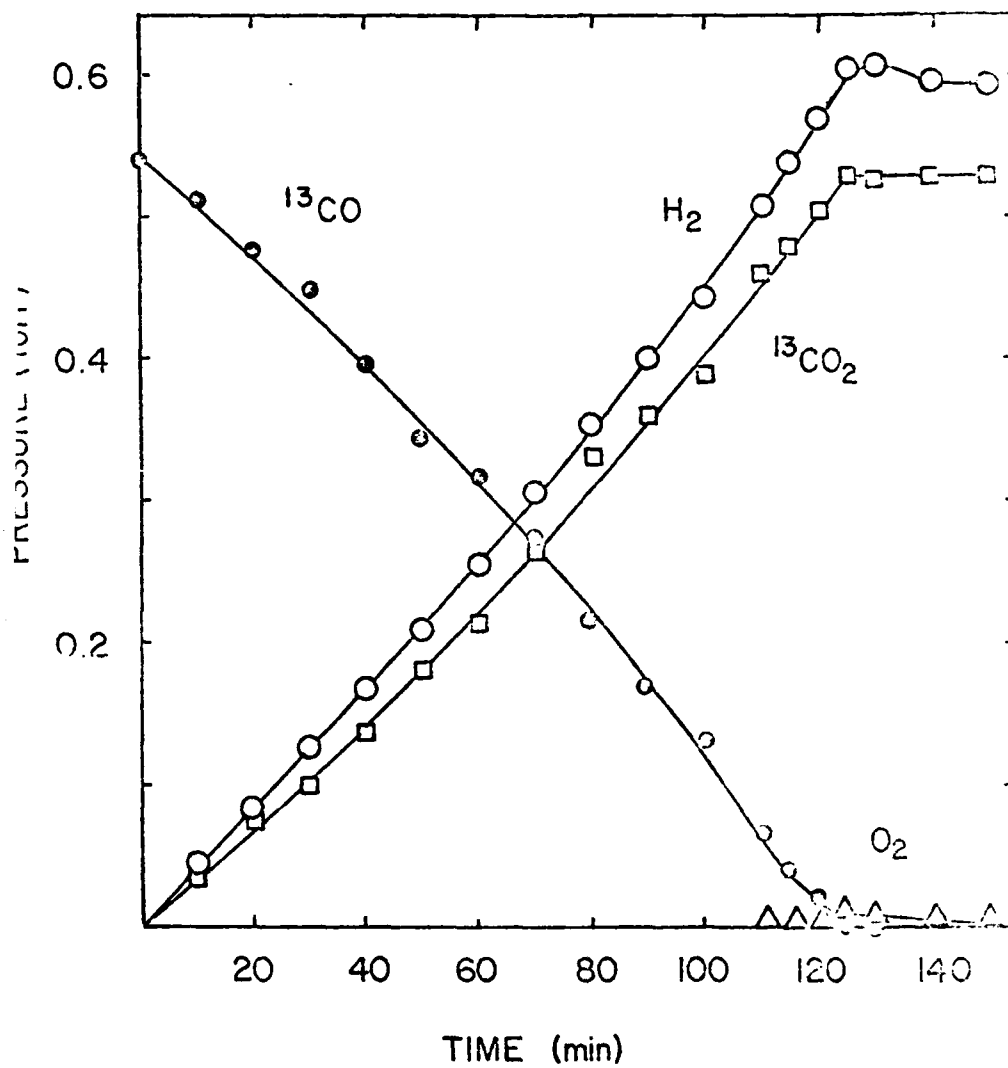
Figure 8

Pictorial Model of the photoinduced redox processes occurring at the Pt/TiO_2 surface.

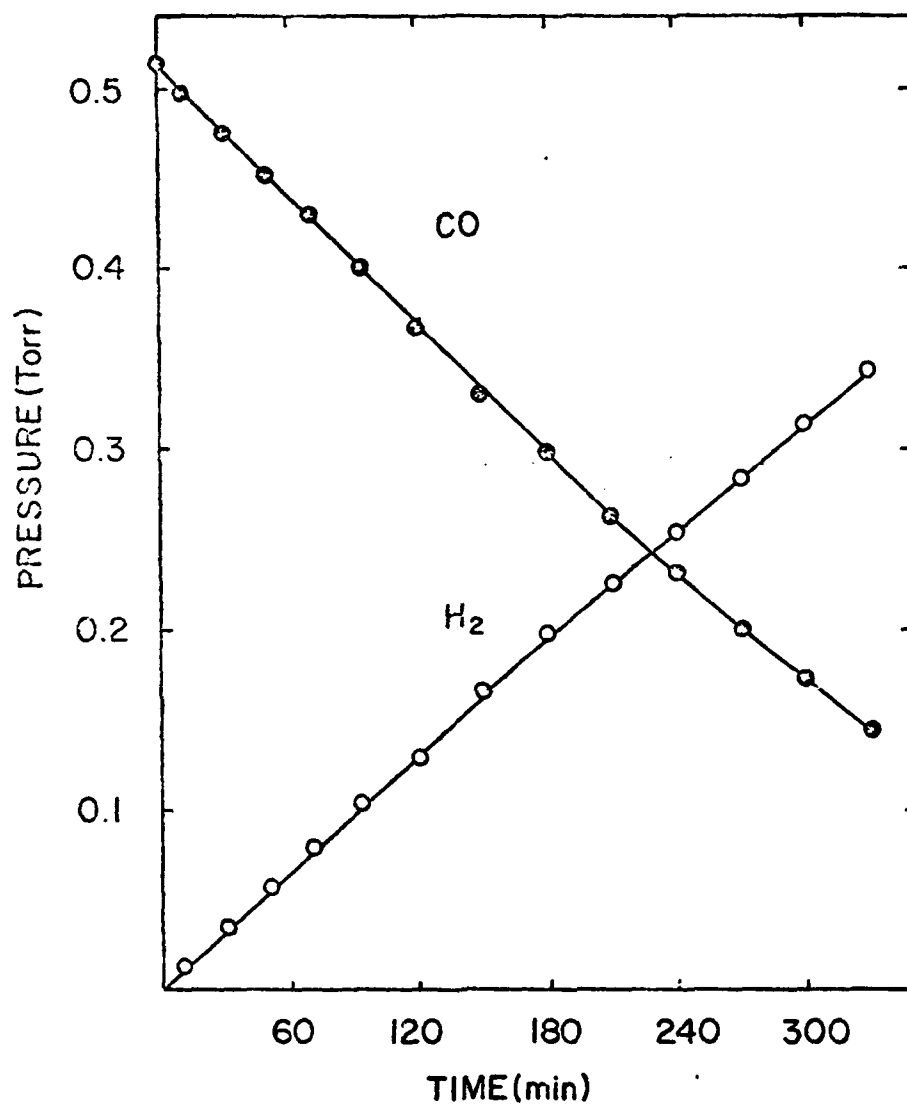


Sato et al. 1984, Fig. 1

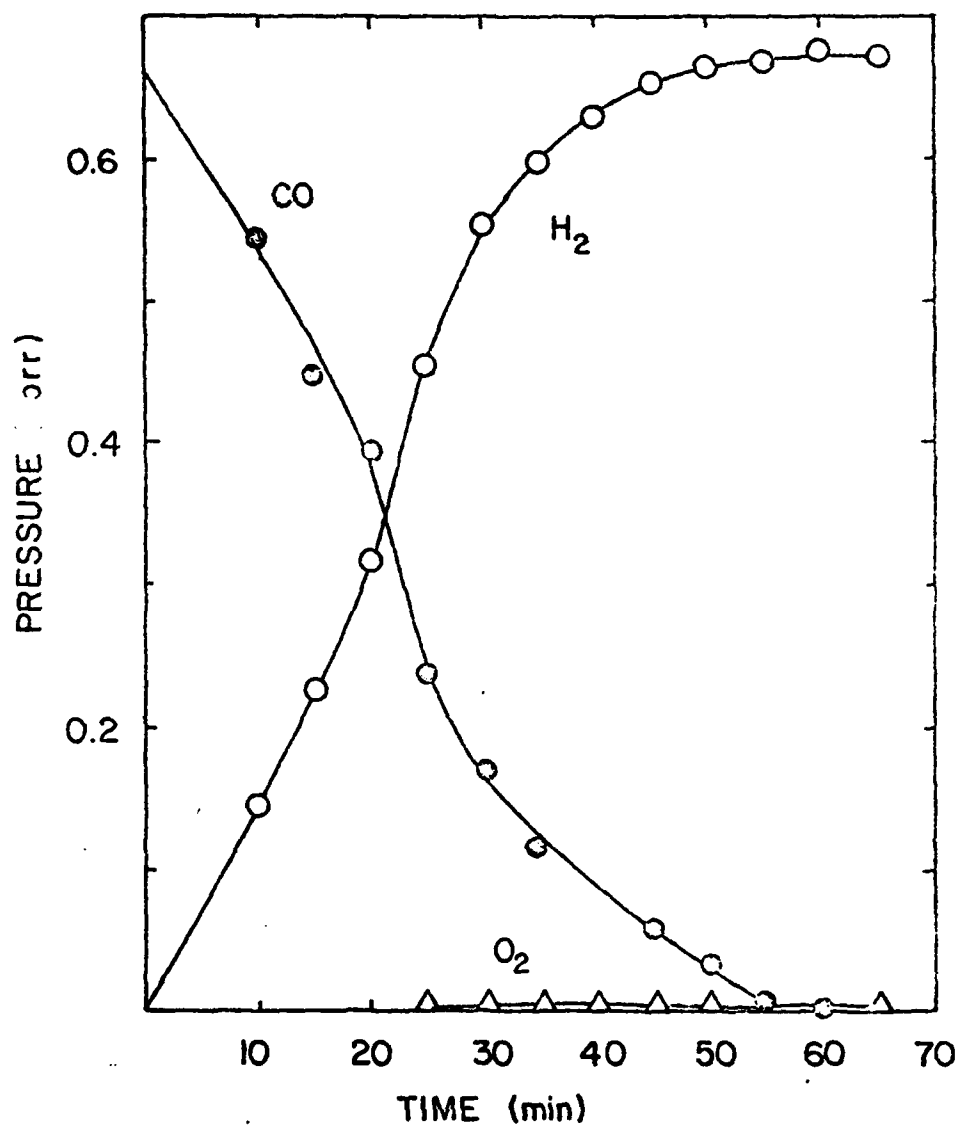
DIFFUSION (Torr)



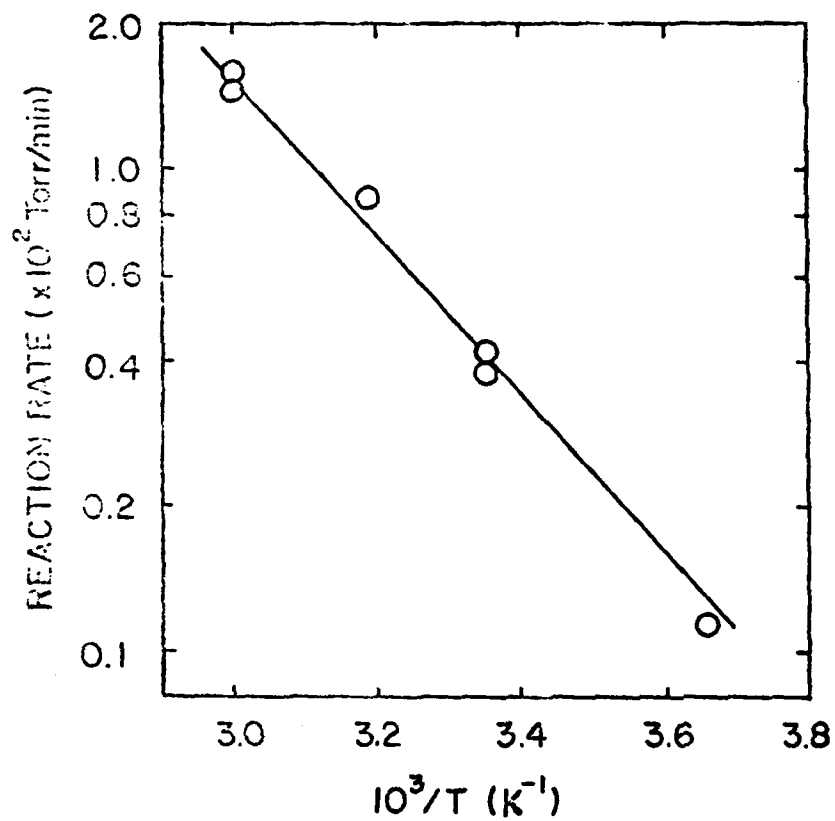
Sato & White, Fig 2.



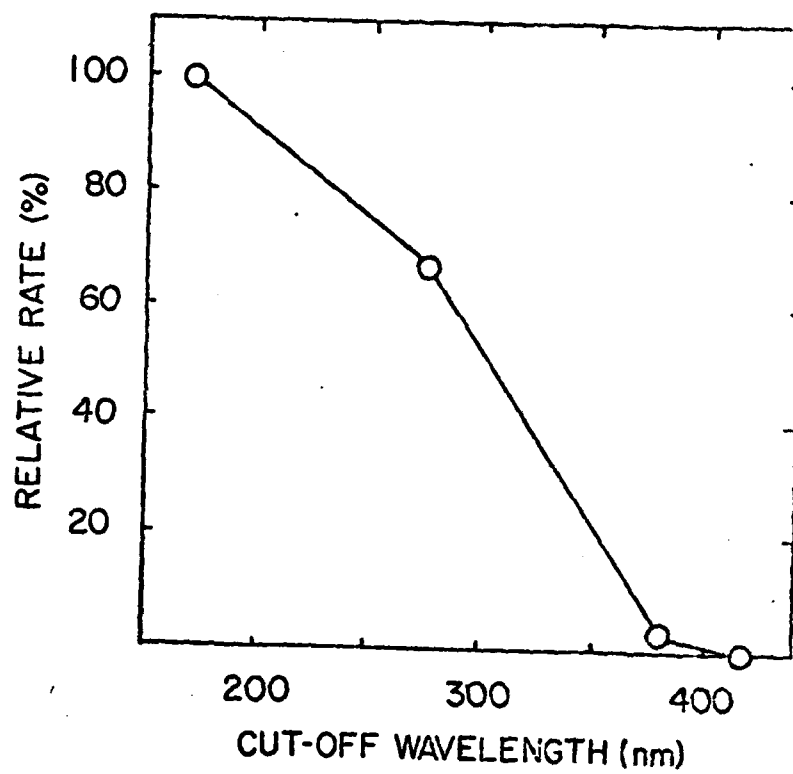
Sato and White, Fig. 3.



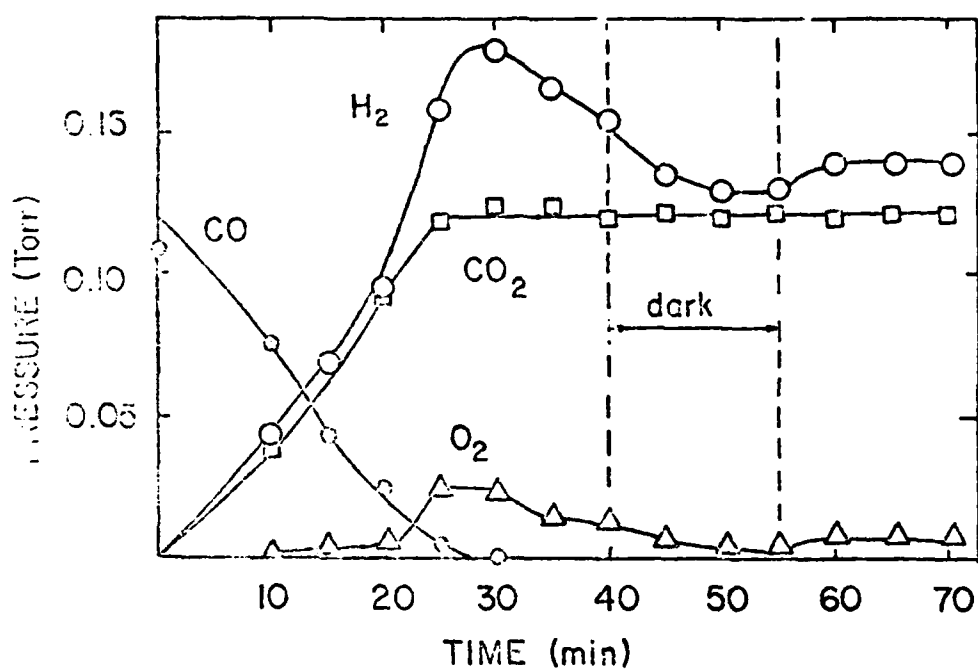
sato & white, fig. 4.



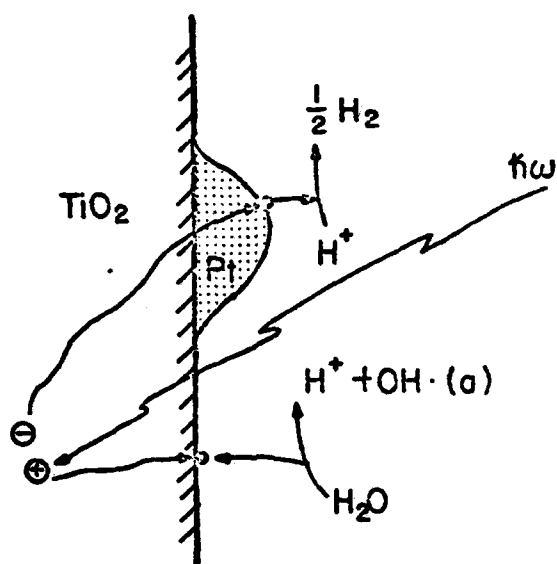
Sato and White, Fig. 5



Sato and Winitz, Fig. 6



data white, Fig. 7.



Sato and White, Fig. 8

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